

**Ethanolic Cosmetic Preparations Containing Chitosan**

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**Field of the Invention**

This invention relates generally to cosmetic preparations and more particularly to formulations which have high ethanol contents and contain special chitosan salts.

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**Prior Art**

Their moisturizing and film-forming properties make chitosans valuable raw materials for the production of cosmetic preparations. Since the chitosans are not water-soluble on their own, they are normally dissolved in a cosmetically acceptable acid, preferably glycolic acid, and marketed in this form. However, the disadvantage of typical commercially obtainable chitosan solutions is that their alcohol compatibility is not high enough so that they are only suitable to a limited extent for the production of sprayable cosmetic preparations of high ethanol content such as, for example, hair sprays or deodorant formulations.

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Reference is made in this connection to European patent application EP 0368253 A2 (Union Carbide) which relates to pharmaceutical preparations for the delayed release of active principles which contain neutralization products of chitosan with various carboxylic acids.

Accordingly, the problem addressed by the present invention was to provide new cosmetic preparations which would contain chitosans in a particularly alcohol-compatible form.

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**Description of the Invention**

The present invention relates to alcohol-based cosmetic preparations containing

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(a) 70 to 90% by weight of ethanol and

(b) 0.01 to 5% by weight of neutralization products of chitosan with lactic acid, pyrrolidone carboxylic acid, nicotinic acid, hydroxyisobutyric acid, hydroxyisovaleric acid and mixtures thereof

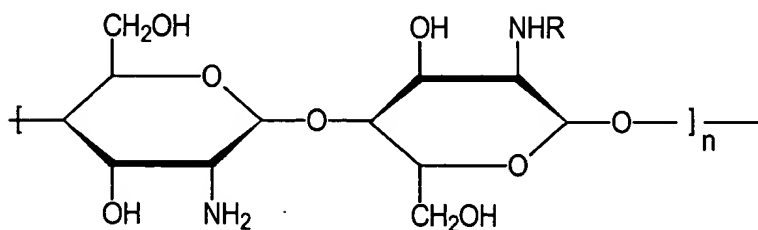
with the proviso that the quantities shown add up to 100% by weight with water and optionally other auxiliaries and additives. If the preparations are sprayed using propellant gases, the ratio by weight of the alcohol-based preparations to the propellant gases may be from 35:65 to 45:55.

It has surprisingly been found that the special chitosan salts are distinguished by greatly improved ethanol compatibility and, accordingly, now allow the production of predominantly alcohol-based formulations such as, for example, hair sprays, hair gels and deodorant formulations. Hair sprays distinguished from known products by a clearly improved setting effect are obtained in this way. So far as hair gels are concerned, the preparations obtained may even be cutting-resistant in terms of consistency, depending on the quantity of chitosans used, so that there is no need to use thickeners. With regard to aerosol formulations, it is possible in accordance with the invention to produce compositions which show relatively high dermatological compatibility and which, in addition, do not stress the hair, but instead counteract dandruff and split ends.

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*Detailed Description of the Invention*  
Chitosan salts

Chitosans are biopolymers which belong to the group of hydrocolloids. Chemically, they are partly deacetylated chitins differing in their molecular weights which contain the following – idealized – monomer unit:



In contrast to most hydrocolloids, which are negatively charged at biological pH values, chitosans are cationic biopolymers under these conditions. The positively charged chitosans are capable of interacting with oppositely charged surfaces and are therefore used in cosmetic hair-care and body-care products and pharmaceutical preparations (cf. **Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A6, Weinheim, Verlag Chemie, 1986, pages 231-332**). Overviews of this subject have also been published, for example, by B. Gesslein et al. in **HAPPI 27, 57 (1990)**, O. Skaugrud in **Drug Cosm. Ind. 148, 24 (1991)** and E. Onsoyen et al. in **Seifen-Öle-Fette-Wachse 117, 633 (1991)**. Chitosans are produced from chitin, preferably from the shell residues of crustaceans which are available in large quantities as inexpensive raw materials. In a process described for the first time by Hackmann et al., the chitin is normally first deproteinized by addition of bases, demineralized by addition of mineral acids and, finally, deacetylated by addition of strong bases, the molecular weights being distributed over a broad spectrum. Corresponding processes are known, for example, from **Makromol. Chem. 177, 3589 (1976)** or French patent application **FR 2701266 A1**. Preferred types are those which are disclosed in German patent applications **DE 4442987 A1** and **DE 19537001 A1** (Henkel) and which have an average molecular weight of either 10,000 to 1,000,000 dalton or 100,000 to 5,000,000 dalton, a Brookfield viscosity (1% by weight in glycolic acid) below 5,000 mPas, a degree of deacetylation of 80 to 88% and an ash content of less than 0.3% by weight. The chitosans are used in the form of 1 to 10% by weight and preferably 2 to 5% by weight dilute solutions in lactic acid, pyrrolidone carboxylic acid, nicotinic acid, hydroxyisobutyric acid, hydroxyisovaleric acid and mixtures thereof and are then present as salts, i.e. as lactates, pyrrolidone carboxylates, nicotines, hydroxybutyrates and/or hydroxyisovalerates.

### Commercial Applications

The preparations according to the invention, which are preferably sprayable products, such as hair treatments (especially hair sprays) or deodorant formulations and also gels, may contain mild surfactants, oil  
5 components, emulsifiers, superfatting agents, pearlizing waxes, stabilizers, consistency factors, thickeners, cationic polymers, silicone compounds, biogenic agents, antidandruff agents, film formers, preservatives, hydrotropes, solubilizers, UV protection factors, insect repellents, self-tanning agents, propellant gases, perfume oils, dyes and the like.

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Typical examples of suitable mild, i.e. particularly dermatologically compatible, **surfactants** are fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or dialkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid  
15 glutamates, ether carboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkyl amidobetaines and/or protein fatty acid condensates (preferably based on wheat proteins).

Suitable **oil components** are, for example, Guerbet alcohols based on fatty alcohols containing 6 to 18 and preferably 8 to 10 carbon atoms, esters of linear C<sub>6-22</sub> fatty acids with linear C<sub>6-22</sub> fatty alcohols, esters of  
20 branched C<sub>6-13</sub> carboxylic acids with linear C<sub>6-22</sub> fatty alcohols, esters of linear C<sub>6-22</sub> fatty acids with branched alcohols, more particularly 2-ethyl hexanol, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or  
25 Guerbet alcohols, triglycerides based on C<sub>6-10</sub> fatty acids, liquid mono-/di-/triglyceride mixtures based on C<sub>6-18</sub> fatty acids, esters of C<sub>6-22</sub> fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, more particularly benzoic acid, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear C<sub>6-22</sub> fatty alcohol carbonates, Guerbet  
30 carbonates, esters of benzoic acid with linear and/or branched C<sub>6-22</sub>

alcohols (for example Finsolv® TN), dialkyl ethers, ring-opening products of epoxidized fatty acid esters with polyols, silicone oils and/or aliphatic or naphthenic hydrocarbons.

Suitable **emulsifiers** are, for example, nonionic surfactants from at least one of the following groups:

- (1) products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group;
- (2) C<sub>12/18</sub> fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide onto glycerin;
- (3) glycerol monoesters and diesters and sorbitan monoesters and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide adducts thereof;
- (4) alkyl mono- and oligoglycosides containing 8 to 22 carbon atoms in the alkyl group and ethoxylated analogs thereof;
- (5) addition products of 15 to 60 moles of ethylene oxide onto castor oil and/or hydrogenated castor oil;
- (6) polyol esters and, in particular, polyglycerol esters such as, for example, polyglycerol polyricinoleate or polyglycerol poly-12-hydroxystearate. Mixtures of compounds from several of these classes are also suitable;
- (7) products of the addition of 2 to 15 moles of ethylene oxide onto castor oil and/or hydrogenated castor oil;
- (8) partial esters based on linear, branched, unsaturated or saturated C<sub>6/22</sub> fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example

cellulose);

(9) trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates;

(10) wool wax alcohols;

(11) polysiloxane/polyalkyl polyether copolymers and corresponding  
5 derivatives;

(12) mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol  
according to **DE 11 65 574 PS** and/or mixed esters of fatty acids  
containing 6 to 22 carbon atoms, methyl glucose and polyols,  
preferably glycerol,

10 (13) polyalkylene glycols and

(14) glycerol carbonate.

The addition products of ethylene oxide and/or propylene oxide onto  
fatty alcohols, fatty acids, alkylphenols, glycerol monoesters and diesters  
and sorbitan monoesters and diesters of fatty acids or onto castor oil are  
15 known, commercially available products. They are homolog mixtures of  
which the average degree of alkoxylation corresponds to the ratio between  
the quantities of ethylene oxide and/or propylene oxide and substrate with  
which the addition reaction is carried out. C<sub>12/18</sub> fatty acid monoesters and  
diesters of addition products of ethylene oxide onto glycerol are known as  
20 refatting agents for cosmetic preparations from **DE 20 24 051 PS**.

C<sub>8/18</sub> alkyl mono- and oligoglycosides, their production and their use  
as surfactants are known, for example, from **US 3,839,318**, **US 3,707,535**,  
**US 3,547,828**, **DE-OS 19 43 689**, **DE 20 36 472 OS** and **DE 30 01 064 A1**  
and also from **EP 0 077 167 A1**. They are produced in particular by  
25 reaction of glucose or oligosaccharides with primary alcohols containing 8  
to 18 C atoms. So far as the glycoside component is concerned, both  
monoglycosides, in which a cyclic sugar unit is attached to the fatty alcohol  
by a glycoside linkage, and oligomeric glycosides with a degree of  
oligomerization of preferably up to about 8 are suitable. The degree of  
30 oligomerization is a statistical mean value on which a homolog distribution

typical of such technical products is based.

Zwitterionic surfactants may also be used as emulsifiers. Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as the N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known by the CTFA name of *Cocamidopropyl Betaine* is particularly preferred. Other suitable emulsifiers are ampholytic surfactants. Ampholytic surfactants are surface-active compounds which, in addition to a C<sub>8/18</sub> alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO<sub>3</sub>H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethyl aminopropionate and C<sub>12/18</sub> acyl sarcosine. Besides ampholytic emulsifiers, quaternary emulsifiers may also be used, those of the esterquat type, preferably methyl-quaternized difatty acid triethanolamine ester salts, being particularly preferred.

**Superfating agents** may be selected from such substances as, for example, lanolin and lecithin and also polyethoxylated or acylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty

acid alkanolamides, the fatty acid alkanolamides also serving as foam stabilizers.

Suitable **pearlizing waxes** are, for example, alkylene glycol esters, especially ethylene glycol distearate; fatty acid alkanolamides, especially cocofatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polybasic, optionally hydroxysubstituted carboxylic acids with fatty alcohols containing 6 to 22 carbon atoms, especially long-chain esters of tartaric acid; fatty compounds, such as for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates which contain in all at least 24 carbon atoms, especially laurone and distearylether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring opening products of olefin epoxides containing 12 to 22 carbon atoms with fatty alcohols containing 12 to 22 carbon atoms and/or polyols containing 2 to 15 carbon atoms and 2 to 10 hydroxyl groups and mixtures thereof.

The **consistency factors** mainly used are fatty alcohols or hydroxyfatty alcohols containing 12 to 22 and preferably 16 to 18 carbon atoms and also partial glycerides. A combination of these substances with alkyl oligoglucosides and/or fatty acid-N-methyl glucamides of the same chain length and/or polyglycerol poly-12-hydroxystearates is preferably used. Suitable **thickeners** are, for example, polysaccharides, more especially xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethyl cellulose and hydroxyethyl cellulose, also relatively high molecular weight polyethylene glycol monoesters and diesters of fatty acids, polyacrylates (for example Carbopols® [Goodrich] or Synthalens® [Sigma]), polyacrylamides, polyvinyl alcohol and polyvinyl pyrrolidone, surfactants such as, for example, ethoxylated fatty acid glycerides, esters of fatty acids with polyols, for example pentaerythritol or trimethylol propane, narrow-range fatty alcohol ethoxylates or alkyl oligoglucosides and electrolytes, such as sodium chloride and ammonium chloride.

Suitable **cationic polymers** are, for example, cationic cellulose derivatives such as, for example, the quaternized hydroxyethyl cellulose obtainable from Amerchol under the name of Polymer JR 400®, cationic starch, copolymers of diallyl ammonium salts and acrylamides, quaternized vinyl pyrrolidone/vinyl imidazole polymers such as, for example, Luviquat® (BASF), condensation products of polyglycols and amines, quaternized collagen polypeptides such as, for example, Lauryldimonium Hydroxypropyl Hydrolyzed Collagen (Lamequat® L, Grünau), quaternized wheat polypeptides, polyethyleneimine, cationic silicone polymers such as, for example, amodimethicone, copolymers of adipic acid and dimethylamino-hydroxypropyl diethylenetriamine (Cartaretine®, Sandoz), copolymers of acrylic acid with dimethyl diallyl ammonium chloride (Merquat® 550, Chemviron), polyaminopolyamides as described, for example, in **FR 2 252 840 A1** and crosslinked water-soluble polymers thereof, cationic chitin derivatives such as, for example, quaternized chitosan, optionally in micro-crystalline distribution, condensation products of dihaloalkyls, for example dibromobutane, with bis-dialkylamines, for example bis-dimethylamino-1,3-propane, cationic guar gum such as, for example, Jaguar®CBS, Jaguar®C-17, Jaguar®C-16 of Celanese, quaternized ammonium salt polymers such as, for example, Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1 of Miranol.

Suitable **silicone compounds** are, for example, dimethyl polysiloxanes, methylphenyl polysiloxanes, cyclic silicones and amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds which may be both liquid and resin-like at room temperature. Typical examples of **fats** are glycerides while suitable **waxes** are inter alia beeswax, carnauba wax, candelilla wax, montan wax, paraffin wax or microwaxes, optionally in combination with hydrophilic waxes, for example cetyl stearyl alcohol or partial glycerides. Metal salts of fatty acids such as, for example, magnesium, aluminium and/or zinc stearate may be

used as **stabilizers**. In the context of the invention, **biogenic agents** are, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts and vitamin complexes. Suitable **antidandruff agents** are climbazol, octopirox and zinc pyrithione. Standard **film formers** are, for example, quaternized chitosan, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, polymers of the acrylic acid series, quaternary cellulose derivatives, collagen, hyaluronic acid and salts thereof and similar compounds.

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10 Suitable **swelling agents** for aqueous phases are montmorillonites, clay minerals, Pemulen and alkyl-modified Carbopol types (Goodrich).

In the context of the invention, **UV protection filters** are organic compounds which are capable of absorbing ultraviolet rays and of releasing the energy absorbed in the form of longer wave radiation, for example heat. Typical examples are 4-aminobenzoic acid and esters and derivatives thereof (for example 2-ethylhexyl-p-dimethylaminobenzoate or p-dimethylaminobenzoic acid octyl ester), methoxycinnamic acid and derivatives thereof (for example 4-methoxycinnamic acid-2-ethylhexyl ester), benzophenones (for example oxybenzone, 2-hydroxy-4-methoxybenzophenone), dibenzoyl methanes, salicylate esters, 2-phenylbenzimidazole-5-sulfonic acid, 1-(4-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione, 3-(4'-methyl)-benzylidenebornan-2-one, methyl-benzylidene camphor and the like. Other suitable UV filters are finely disperse metal oxides and salts, for example titanium dioxide, zinc oxide, iron oxide, aluminium oxide, cerium oxide, zirconium oxide, silicates (talcum) and barium sulfate. The particles should have an average diameter of less than 100 nm, preferably from 5 to 50 nm and more preferably from 15 to 30 nm. They may be spherical in shape although ellipsoidal particles or other non-spherical particles may also be used. Besides the two above-mentioned groups of primary light filters,

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secondary light filters of the antioxidant type, which interrupt the photochemical reaction chain initiated when UV radiation penetrates into the skin, may also be used. Typical examples of these secondary light filters are Superoxid-Dismutase, tocopherols (vitamin E) and ascorbic acid (vitamin C).

In addition, **hydrotropes**, such as, for example, ethanol, isopropyl alcohol or polyols may be used to improve flow behavior. Suitable polyols preferably contain 2 to 15 carbon atoms and at least two hydroxyl groups. Typical examples are

- glycerol;
- alkylene glycols such as, for example, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and polyethylene glycols having an average molecular weight of 100 to 1,000 dalton;
- technical oligoglycerol mixtures with a degree of self-condensation of 1.5 to 10 such as, for example, technical diglycerol mixtures with a diglycerol content of 40 to 50% by weight;
- methylol compounds such as, in particular, trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythritol and dipentaerythritol;
- lower alkyl glucosides, particularly those containing 1 to 8 carbon atoms in the alkyl group, for example methyl and butyl glucoside;
- sugar alcohols containing 5 to 12 carbon atoms such as, for example, sorbitol or mannitol;
- sugars containing 5 to 12 carbon atoms such as, for example, glucose or sucrose and
- aminosugars such as, for example, glucamine.

Suitable **preservatives** are, for example, phenoxyethanol, formaldehyde solution, parabens, pentanediol or sorbic acid. Suitable **insect repellents** are N,N-diethyl-m-toluamide, pentane-1,2-diol or Insect

Repellent 3535. A suitable **self-tanning agent** is dihydroxyacetone. Suitable **propellent gases** are dimethylether and aliphatic hydrocarbons and mixtures thereof.

Suitable **perfume oils** include the extracts of blossoms (lavender, rose, jasmine, neroli), stems and leaves (geranium, patchouli, petitgrain), fruits (anise, coriander, caraway, juniper), fruit peel (bergamot, lemon, orange), roots (nutmeg, angelica, celery, cardamon, costus, iris, calmus), woods (sandalwood, guaiac wood, cedarwood, rosewood), herbs and grasses (tarragon, lemon grass, sage, thyme), needles and branches (spruce, fir, pine, dwarf pine), resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Animal raw materials, for example civet and beaver, may also be used. Suitable synthetic or semisynthetic perfume oils are Ambroxan, eugenol, isoeugenol, citronellal, hydroxycitronellal, geraniol, citronellol, geranyl acetate, citral, ionone and methyl ionone.

Suitable **dyes** are any of the substances suitable and approved for cosmetic purposes as listed, for example, in the publication "**Kosmetische Färbemittel**" of the **Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pages 81 to 106**. These dyes are normally used in concentrations of 0.001 to 0.1% by weight, based on the mixture as a whole.

The total percentage content of auxiliaries and additives may be from 1 to 50% by weight and is preferably from 5 to 40% by weight, based on the particular formulation. The formulations may be prepared by standard cold or hot processes and are preferably produced by the phase inversion temperature method.

### Examples

The preparations according to the invention have many advantages by virtue of their high ethanol content and the presence of the ethanol-

compatible chitosan salts. For example, investigations of keratin fibers have shown that an aqueous preparation containing 0.2% by weight of chitosan glycolate achieves a flexural strength of 50% while the same preparation containing 0.2% by weight of chitosan hydroxyisovalerate and 90% by weight ethanol achieves 110% setting. For comparison: if the chitosan hydroxyisovalerate is replaced by a known film former of the vinyl pyrrolidone/vinyl acetate copolymer type, only 60% setting is achieved. The ethanol compatibility of various chitosan salts is shown in the following Table:

**Table 1.**

Ethanol compatibility of chitosan salts

Chitosan salt	Ethanol compatibility
Chitosan aspartate	50
Chitosan glutamate	55
Chitosan azelate	60
Chitosan glycolate	65
Chitosan pyrrolidone carboxylate	70
Chitosan lactate	80
Chitosan nicotinate	80
Chitosan hydroxyisobutyrate	95
Chitosan hydroxyisovalerate	95